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The effect of calcium and praseodymium deficiencies on the physical properties of $Pr_{0.5}Ca_{0.5}MnO_3$

I. Walha[a]*, A. Cheikhrouhou[a]

[a]*Laboratoire de Physique des Matériaux, Faculté des Sciences de Sfax, B. P. 1171, Sfax, Tunisia.*

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Abstract

Structural and magnetic properties of small amount 5% of praseodymium and calcium deficiency of polycrystalline $Pr_{0.5}Ca_{0.5}MnO_3$ manganite have been investigated. Our synthesized samples have been elaborated using the conventional solid state reaction at high temperature. Rietveld refinements of the X-ray diffraction patterns show that all our samples are single phase and crystallize in the orthorhombic structure with Pnma space group. Praseodymium deficiency leads to a decrease of the unit cell volume while calcium deficiency leads to an increase of the unit cell volume. Magnetization measurements show that the magnetic properties depend strongly on the nature of the deficiency.

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Keywords: Manganites, Ferromagnetism, Curie temperature

1. Introduction

Doped perovskite manganites R1-xAxMnO3 where R and A respectively trivalent rare earth and divalent alkali-earth elements have attracted considerable attention during the last decade for their interesting physical properties such as colossal magnetoresistance CMR, charge ordering (CO) and orbital ordering (OO) [1-6]. The charge ordering (CO) state is generally associated with antierromagnetic (AFM) and insulating behavior [7] is observed in Pr1-xCaxMnO3 perovskite over a large composition range of $0.3<x<0.9$ [8]. Furthermore, $Pr_{0.5}Ca_{0.5}MnO_3$ show charge-ordering/ orbital ordering state for temperature below 230K, and antiferromagnetic (AFM) insulator state below T_N=180 K [9]. The deviation of the Mn^{3+}/Mn^{4+} ratio away from unity, hence destabilizing the CO phase. The ionic size mismatch lead to changes in the magnetic state [10-11]. Charge ordering can be induced by reducing the bandwidth owing to its origin to coulomb repulsion, orbital ordering and Jahn Teller distortion. Here we report on the structural and magnetic properties of small amount of Pr and Ca deficiency of half doped $Pr_{0.5}Ca_{0.5}MnO_3$. In such systems, the praseodymium and calcium vacancies imply an increase of the Mn^{4+} content beyond 50% and also a change in the average radius $\langle r_A \rangle$ of the A site.

* Corresponding author. Tel.: +0-000-000-0000 ; fax: +0-000-000-0000 .
E-mail address: skander_walha@yahoo.fr.

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2. Experimental

Powder samples of $Pr_{0.5-x}\square_xCa_{0.5}MnO_3$ and $Pr_{0.5}Ca0.5–x\square_xMnO_3$ have been elaborated by conventional solid state reaction mixing Pr_6O_{11}, Mn_2O_3 and $CaCO_3$ up to 99.9% purity in the desired proportion according to the following reactions:

$$0.5\ Pr_6O_{11} + 6(0.5\text{-}x)\ CaCO_3 + 3Mn_2O_3 \rightarrow 6\ Pr_{0.5}Ca_{0.5-x}\square_xMnO_3 + \delta\ CO_2$$

$$(0.5\text{-}x)\ Pr_6O_{11} + 3CaCO_3 + 3Mn_2O_3 \rightarrow 6\ Pr_{0.5-x}\square_xCa_{0.5}MnO_3 + \delta\ CO_2$$

The starting materials are mixed in an agate mortar and then heated in air at 1000°C for 60 hours. Systematic annealing at high temperature is necessary to ensure a complete reaction. In fact, the powders are pressed into pellets (of about 1mm thickness) and sintered at 1350°C in air for 60hours with intermediate regrinding and repelling. Finally these pellets are rapidly quenched in water.

Phase purity, homogeneity, and cell dimensions have been determined by powder X-ray diffraction at room temperature (with Mokα_1 radiation). Unit cell dimensions are obtained by least-squares calculations.

Magnetization measurements versus temperature in the range of (5-300 K) and field (up to 8 Tesla) were recorded on a SQUID magnetometer.

3. Resultats and discussions

A praseodymium and calcium vacancy in our samples implies a partial conversion of Mn^{3+} to Mn^{4+} above 50%. According to the general formula, the Mn tetravalent and trivalent contents are (0.5+3x) and (0.5-3x) in the praseodymium deficient and (0.5+2x) and (0.5-2x) in the calcium deficient ones. This vacancy leads also to a change in the average ionic radius $<r_A>$ of the A site. The Mn^{3+} and Mn^{4+} contents have been checked by chemical analysis. We list in table1 the chemical analysis results. The experimental results agree with the theoretical data and confirmed the amount of deficiency in our lacunar samples.

Table 1. Chemical analysis results for the $Pr_{0.5}Ca_{0.5}MnO_3$, $Pr_{0.5}Ca_{0.45}\square_{0.05}MnO_3$ and $Pr_{0.45}\square_{0.05}Ca_{0.5}MnO_3$ samples.

Samples	%Mn^{4+}theoretical	%Mn^{4+}experimental
$Pr_{0.5}Ca_{0.5}MnO_3$	50	50.85
$Pr_{0.45}\square_{0.05}Ca_{0.5}MnO_3$	65	63.95
$Pr_{0.5}Ca_{0.45}\square_{0.05}MnO_3$	60	59.60

X-ray diffraction patterns at room temperature showed that our samples are in a single phase. Rietveld refinement [12] of the X-ray data was carried out using the FULLPROF code [13]. This program permits multiple phase refinements of each coexisting phase. The quality of the refinement is evaluated through several parameters: the pattern R factor (R_f) and the goodness-of-fit indicator (χ^2). No unfitted peaks were observed in the difference pattern, indicating that less 1% of the second phase was present in our samples. In the orthorhombic structure, the MnO_6 octahedral are distorted and rotated from the ideal perovskite orientation. Pr/Ca atoms were located at 4c (x, y, 0.25) positions, Mn atoms at 4a (0, 0, 0) and oxygen atoms occupy two different sites, namely O1 at 4c (x, y, 0.25) and O2 at 8d (x, y, z) positions. The Mn atom is coordinated by six oxygen atoms forming an irregular octahedron. Fig 1 shows the crystal structure of $Pr_{0.5}Ca_{0.5}MnO_3$ and the coordination polyhedron for Mn and the distances between Mn and the first neighbour oxygen's.

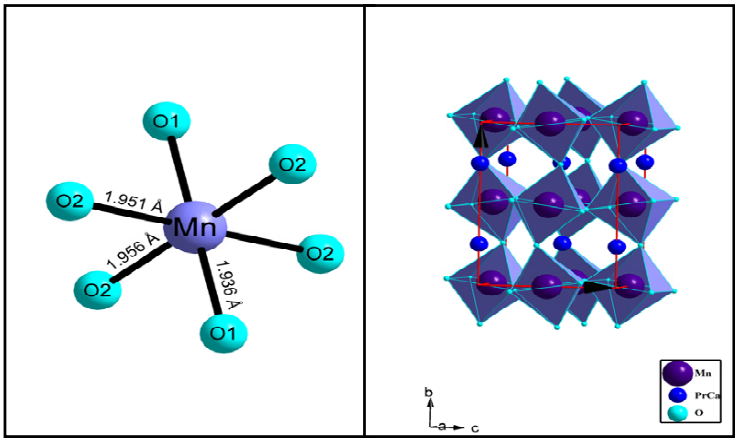


Fig.1. Crystal structure of $Pr_{0.5}Ca_{0.5}MnO_3$ and the coordination polyhedron on Mn

Details of structural data for all samples are summarized in table 2. A good fit between the observed and the calculated profiles was obtained, as shown in Fig 2. Praseodymium deficiency leads to reduce the unit cell volume whereas calcium deficiency leads to an increase of the unit cell volume. This result can be explained by the difference in the average ionic radius $<r_V>$ of the lacuna and for electrostatic consideration, a vacancy must have an average radius $<r_V>\neq 0$.

Table 2. Refined structural parameters of $Pr_{0.5}Ca_{0.5}MnO_3$, $Pr_{0.5}Ca_{0.45}\square_{0.05}MnO_3$ and $Pr_{0.45}\square_{0.05}Ca_{0.5}MnO_3$ samples at room temperature.

Parameter	$Pr_{0.5}Ca_{0.5}MnO_3$	$Pr_{0.45}{}_{0.05}Ca_{0.5}MnO_3$	$Pr_{0.5}Ca_{0.45}{}_{0.05}MnO_3$
a (Å)	5. 4034(7)	5. 4059(4)	5.4169(5)
b (Å)	7. 6190(3)	7. 6214(0)	7.6304(4)
c(Å)	5. 4006(4)	5. 4015(6)	5.4083(9)
V($Å^3$)	223. 24(4)	222. 22(4)	223. 54(8)
Mn-O1(Å)	1.936(3)	1.967(3)	1.953(5)
Mn-O2(Å)	1.956(2)	1.9603(2)	1.947(4)
Mn-O2(Å)	1.951(6)	1.9521	1.936(6)
Mn-O1-Mn(°)	157. 9(3)	157. 1(5)	158. 9(5)
Mn-O2-Mn(°)	158. 5(9)	158. 0(8)	159. 3(4)
(χ^2)	1.3%	1.6%	2%

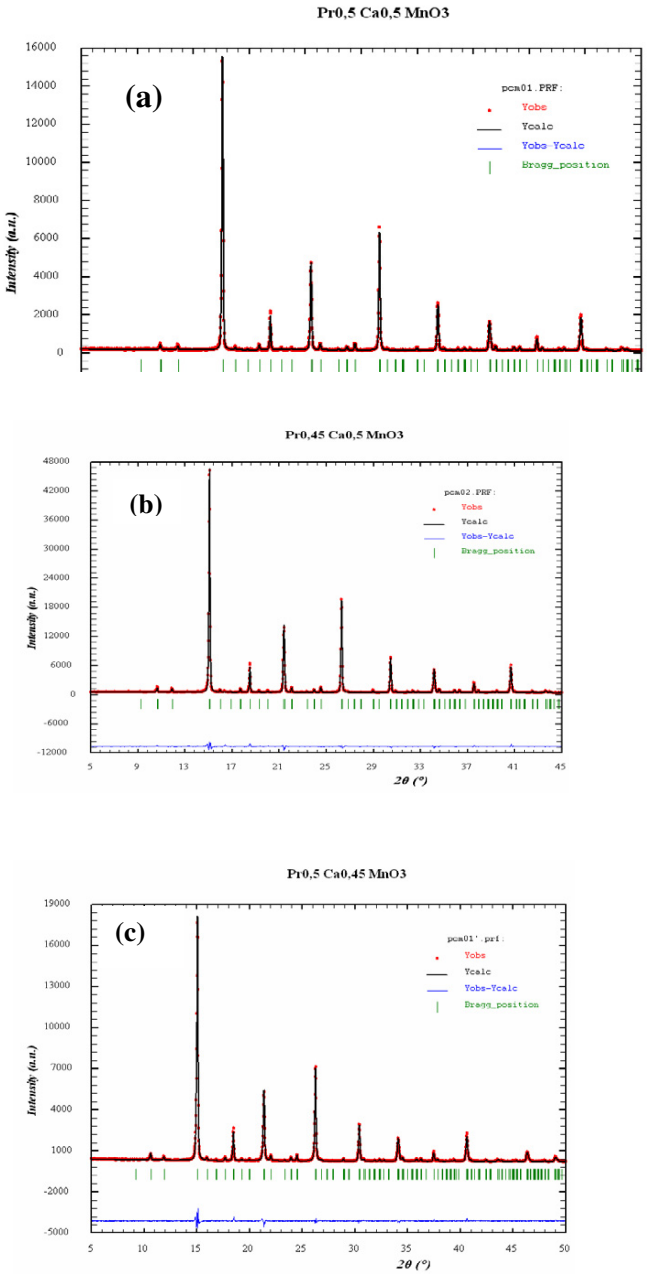


Fig. 2. XRD patterns of (a) $Pr_{0.5}Ca_{0.5}MnO_3$, (b) $Pr_{0.45\ \ 0.05}Ca_{0.5}MnO_3$ and (c) $Pr_{0.5}Ca_{0.45\ \ 0.05}MnO_3$ compounds.

The powder X-ray diffraction patterns obtained at temperature between 300K and 90K in air for $Pr_{0.5}Ca_{0.5}MnO_3$ are shown in Fig.3. The fundamental peaks in the diffraction patterns between room temperature and 90 K are obviously identical. Thus, no phase transition was detected. The observed, calculated and difference profiles after refinement are shown in Fig.4 for T=90 K.

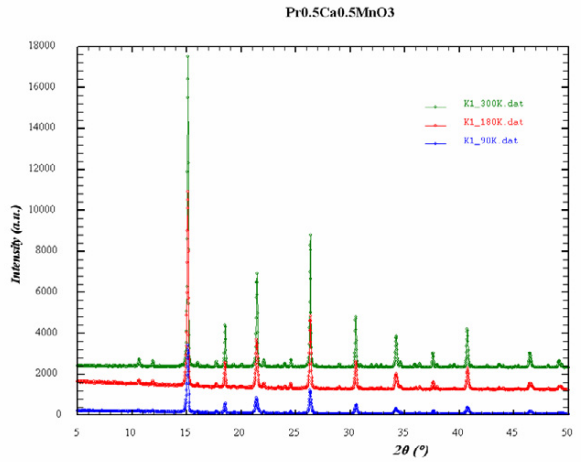


Fig. 3. Powder X-ray diffraction patterns for $Pr_{0.5}Ca_{0.5}MnO_3$ at several temperatures.

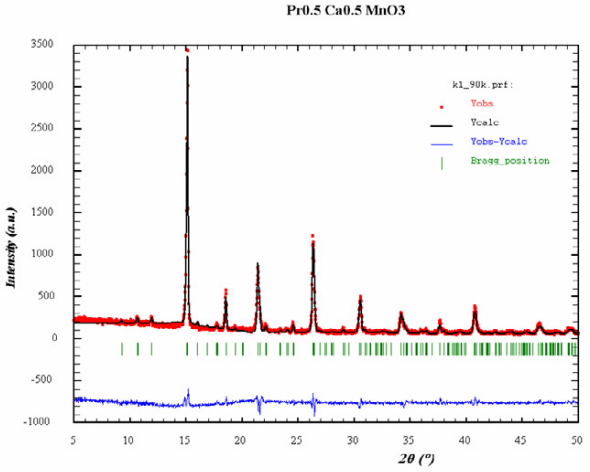
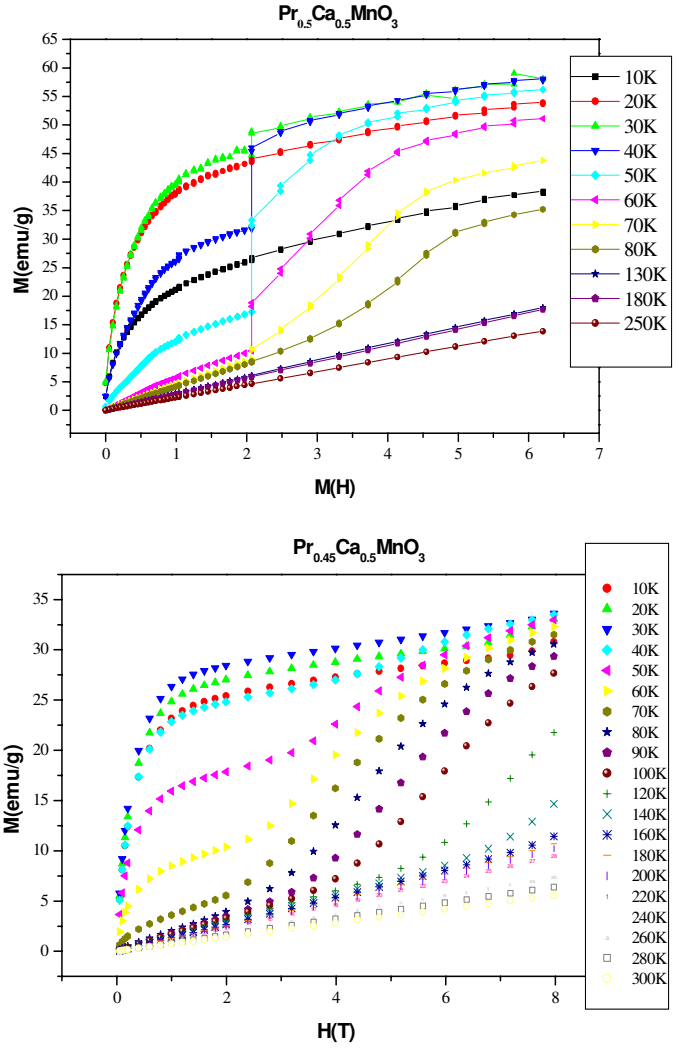


Fig. 4. XRD pattern for $Pr_{0.5}Ca_{0.5}MnO_3$ at 90K.

We report in Fig.5 the evolution of the magnetization versus applied field up to 8 T at several temperatures for $Pr_{0.5}Ca_{0.5}MnO_3$, $Pr_{0.45\ 0.05}Ca_{0.5}MnO_3$ and $Pr_{0.5}Ca_{0.45\ 0.05}MnO_3$ compounds. For the stoichiometric compound $Pr_{0.5}Ca_{0.5}MnO_3$ three humps were seen around 40, 50 and 60 K with increasing magnetic field above 2 T indicate the antiferromagnetic ordering of Mn spin [2,18]. For the praseodymium deficient sample the humps disappear and it behaves as a ferromagnetic material at low temperature (20 K). This compound exhibits a metamagnetic behaviour in the temperature range [100-60 K]. Calcium deficiency sample exhibits a metamagnetic behaviour at low temperatures (20K). 5% of Ca-deficient destroys the ferromagnetic behaviour observed in the parent compound, while 5% of Pr- deficient reinforces the ferromagnetic behaviour observed in the parent compound. The magnetization decrease in the both deficiencies compounds can be explained by the increase of the Mn^{4+} content, which leads to a weakness of the double exchange interactions.



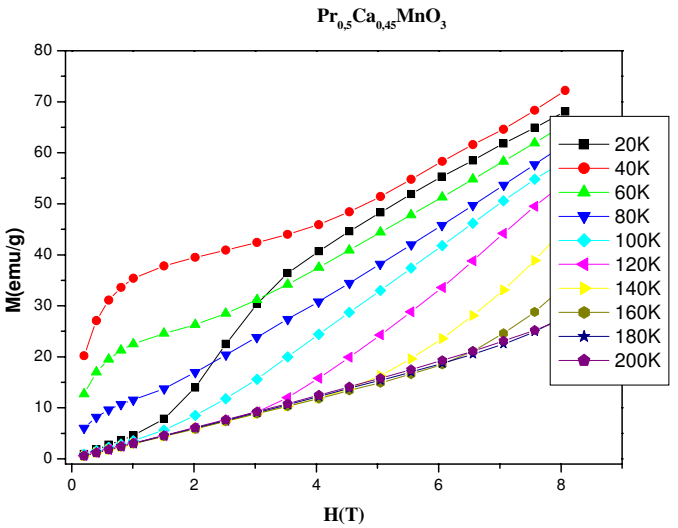


Fig. 5. The evolution of the magnetization versus applied field up to 8T at several temperatures for $Pr_{0.5}Ca_{0.5}MnO_3$, $Pr_{0.45}{}_{0.05}Ca_{0.5}MnO_3$ and $Pr_{0.5}Ca_{0.45}{}_{0.05}MnO_3$ samples

4. Conclusion

We elaborate and investigate the structural and magnetic properties of small amount 5% of praseodymium and calcium deficiency of $Pr_{0.5}Ca_{0.5}MnO_3$, Our synthesized samples crystallize in the orthorhombic structure with Pnma space group. The effect of Ca and Pr deficiency on the physical properties of $Pr_{0.5}Ca_{0.5}MnO_3$ depends strongly on the nature of the deficiency.

Acknowledgment

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